

PTO 11-4442

CC=JP
DATE=20020719
KIND=A
PN=2002201202

CATIONIZED CARBOXYMETHYL CELLULOSE SODIUM SALT
[KACHIONKA KARUBOKISHIMECHIRUSERUROOSUNATORIUMU EN]

KOJI OSOKAWA, ET AL.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. JUNE 2011
TRANSLATED BY: SCHREIBER TRANSLATIONS, INC.

PUBLICATION COUNTRY	(10) :	JP
DOCUMENT NUMBER	(11) :	2002201202
DOCUMENT KIND	(12) :	A
PUBLICATION DATE	(43) :	20020719
APPLICATION NUMBER	(21) :	2000402566
APPLICATION DATE	(22) :	20001228
INTERNATIONAL CLASSIFICATION	(51) :	C08B 15/04 D06M 15/09 D21H 17/26 21/10
PRIORITY COUNTRY	(33) :	N/A
PRIORITY NUMBER	(31) :	N/A
PRIORITY DATE	(32) :	N/A
INVENTOR(S)	(72) :	KOJI HOSOKAWA NOBUHIRO HANADA
APPLICANT(S)	(71) :	NIPPON PAPER INDUSTRIES CO., LTD.
DESIGNATED CONTRACTING STATES	(81) :	N/A
TITLE	(54) :	CATIONIZED CARBOXYMETHYL CELLULOSE SODIUM SALT
FOREIGN TITLE	[54A] :	KACHIONKA KARUBOKISHIMECHIRUSERUROOSU NATORIUMU EN

[Claims]

[Claim 1] A cationized carboxymethyl cellulose sodium salt, characterized in that the degree of substitution of a carboxymethyl group is in a range of from 0.4 to 2.0 per glucose residue and the degree of substitution of a cationic group is in a range of from 0.01 to 1.0 per glucose residue.

[Claim 2] The cationized carboxymethyl cellulose sodium salt according to Claim 1, characterized in that the degree of substitution of a carboxymethyl group (CM-DS) and the degree of substitution of a cationic group (CT-DS) satisfy the following formula 1:

$$0.01 \leq (CT-DS / CM-DS) \leq 0.5 \dots \text{Formula 1}$$

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The present invention relates to a cationized carboxymethyl cellulose sodium salt (which is referred to simply as "CMC", hereinafter). Cationized CMCs can be used in various forms, examples of which include: a thickening agent; a coagulating agent; a flocculating agent; an adhesion promoter; a dispersion stabilizer; a laundry finishing agent; a muddy water regulating agent; a retention aid for paper making; a drainage improving agent; an antistatic agent for fibers and fabrics; a texture improving agent; a compounding

agent for shampoos, rinses, treatments and the like; and a compounding agent for pastes, adhesive agents, inks and the like.

[0002]

[Prior Art] Conventionally, a carboxymethyl cellulose sodium salt (which is referred to simply as "CMC", hereinafter) has various characteristics of an anionic water-soluble polymer, such as thickening properties, adhesiveness, dispersibility, emulsification stability, protective colloidal properties and film formability, and therefore has been used in various fields, such as food industries, pharmaceutical industries, cosmetic industries, fiber industries and paper manufacturing industries.

[0003] Examples of factors that influence the physical properties of CMCs, such as chemical resistance, dispersion stability, protective colloidal properties and thixotropic properties, include the uniformity of the carboxymethylation reaction. More specifically, the production method for a CMC in accordance with a solvent method generally comprises the following steps of: first reacting cellulose with an alkali in order to prepare alkali cellulose, and adding monochloroacetic acid as an etherifying agent to the resulting alkali cellulose in order to cause an etherification reaction.

[0004] However, when monochloroacetic acid is used as an etherifying agent after the preparation of alkali cellulose, the monochloroacetic acid, which is a strong acid, and the sodium

hydrate in the alkali cellulose, which is a strong alkali, cause a rapid neutralization reaction, thus the resulting heat of neutralization locally increases the temperature in the reaction system, and the etherification reaction proceeds in a non-uniform manner during the addition of the monochloroacetic acid, resulting in the carboxymethyl group being non-uniformly substituted.

[0005] Hence, in order to improve the physical properties of CMCs, such as chemical resistance, dispersion stability, protective colloidal properties and thixotropic properties, attempts have previously been made by conducting the carboxymethylation reaction uniformly (e.g., Japanese Examined Patent Publication No. Showa 60-35361). Japanese Examined Patent Publication No. Showa 60-35361 proposes a method for producing a CMC wherein it uses a monochloroacetic acid ester of isopropyl alcohol (isopropyl monochloroacetate) which is the most commonly used as a reaction solvent for CMCs as an etherifying agent which is relatively stable in an aqueous alcohol solution and has a low hydrolysis rate.

[0006] However, in order to obtain isopropyl monochloroacetate in accordance with the above-described method, the etherification rate may not reach approximately 95% unless monochloroacetic acid is reacted with isopropyl alcohol at a temperature where monochloroacetic acid is boiled in the

presence of a solvent, such as benzene, for a period of 20 hours to 24 hours; therefore, the preparation of the isopropyl monochloroacetate in the above-described method is quite complicated and requires considerable amount of time.

[0007] Further, there is also a method in which sodium monochloroacetate, which is a salt type etherifying agent, is used. Although the heat of neutralization during the addition of the etherifying agent is not caused unlike the addition of monochloroacetic acid, various problems are encountered, such as the etherifying agent being hardly dissolved in a solvent except for water, which reduces the reaction efficiency, and the etherifying agent being expensive.

[0008] Further, Japanese Examined Patent Publication No. Showa 45-20318 proposes a cellulose derivative having both a carboxyl group and a cationic group as a quaternary nitrogen-containing cellulose ether. Unfortunately, the product is unsatisfactory in terms of use as an adhesion promoter or surface improver.

[0009]

[Problem to Be Solved by the Invention] The present invention is an idea aimed at solving the above-mentioned problems of prior art. The object of the present invention is to provide, as a CMC having improved physical properties, a cationized CMC which has excellent properties for use as an adhesion promoter or surface improver.

[0010]

[Means of Solving the Problem] The present inventors conducted intensive research on the physical properties of CMCs, such as chemical resistance, dispersion stability, protective colloidal properties and thixotropic properties, and then discovered that the introduction of a carboxyl group and a cationic group at a specific ratio into cellulose developed physical properties which a CMC that was an anionic water-soluble polymer did not have. The present invention is based on this discovery.

[0011] More specifically, the present invention relates to a cationized CMC, characterized in that the degree of substitution of a carboxymethyl group (CM-DS) is in a range of from 0.4 to 2.0 per glucose residue and the degree of substitution of a cationic group (CT-DS) is in a range of from 0.01 to 1.0 per glucose residue.

[0012]

[Embodiment] The inventive cationized CMC can be produced by any of the following methods: subjecting a CMC as a starting material to a cationization reaction; subjecting cellulose as a starting material to a cationization reaction and then to a carboxymethylation reaction; and subjecting cellulose to the cationization reaction and the carboxymethylation reaction simultaneously. Thus, the carboxymethylation reaction may be

conducted before and after the carboxymethylation reaction or with the carboxymethylation reaction simultaneously .

[0013] Examples of materials for the production of the cellulose in the present invention include: natural cellulose produced by bleached or unbleached pulps, purified linters or microorganisms, such as acetic acid bacteria; regenerated cellulose obtained by dissolving cellulose in a solvent, such as a cuprammonium solution and a morpholine derivative, and then spinning the cellulose again; fine cellulose obtained by subjecting the above-mentioned cellulose material to a depolymerization, such as acid hydrolysis, alkaline hydrolysis, enzymatic degradation, a blasting treatment, or a treatment using a vibration ball mill; and fine cellulose obtained by subjecting the above-mentioned cellulose to a mechanical process.

[0014] Not only can commercially available CMCs which are produced by either a solvent method or a water solvent method be used but also undried and unpurified CMCs obtained by any of the known carboxymethylation methods, such as a method in which the above-mentioned material for the production of cellulose is mercerized by an alkali, such as sodium hydroxide,

/2

and etherifying the resulting product with monochloroacetic acid or sodium monochloroacetate. Further, cationized cellulose can also be carboxymethylated by the same method as above.

[0015] In the present invention, a CMC having a CM-DS of from 0.4 to 2.0 is used. If the degree of substitution of a carboxymethyl group is out of the above-specified range, improvement effects on the adhesion promoting properties and surface improving properties may not be obtained. If the degree of substitution is less than 0.4, the characteristics of the CMC may not be obtained, whereas if the degree of substitution exceeds 2.0, the anionization degree may increase excessively, resulting in the effect by the introduction of a cationic group not being obtained. The degree of substitution is more preferably in a range of from 0.6 to 1.8.

[0016] The cationization reaction is adjusted such that the CT-DS is in a range of from 0.01 to 1.0 by subjecting the above-described cellulose or CMC as a starting material to a mercerization process in a mixture solvent, then adding a cationization agent, in an amount of from 0.01 times mol to 5.0 times mol per glucose residue in the starting material, to the resulting solution, and causing a reaction at a temperature of from 30 degrees Celsius to 90 degrees Celsius, preferably from 40 degrees Celsius to 80 degrees Celsius, for a period of from 30 minutes to 10 hours, preferably from one hour to four hours, said mixture solvent being obtained by mixing a mixture solvent consisting of one or more lower alcohols, such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butanol,

isobutanol, and tertiary butanol, and water with an alkali metal hydroxide, such as sodium hydroxide and potassium hydroxide, in an amount of 0.01 times mol to 15 times mol per glucose residue in the starting material so that the proportion of the lower alcohol as against the total amount of the lower alcohol and water to be in a range of from 75 wt% to 95 wt%.

[0017] Examples of the cationization agent that is used in the present invention include glycidyl trialkyl ammonium halide or its halohydrin form. Specific examples of such compounds include glycidyl trimethyl ammonium chloride, glycidyl triethyl ammonium chloride, glycidyl trimethyl ammonium bromide, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride, and 3-chloro-2-hydroxypropyl trimethyl ammonium bromide. The amount of such a cationization agent added may vary depending on the intended CT-DS value, but is generally in a range of from 0.01 times mol to 5.0 times mol, preferably in a range of from 0.05 times mol to 3.0 times mol, per glucose residue in the starting material cellulose or CMC. If the amount of the cationization agent added is less than 0.01 times mol per glucose residue in the starting material, the degree of substitution of a cationic group to be introduced may be decreased, whereas if the amount of the cationization agent added exceeds 5.0 times mol per glucose residue in the starting material, the cationic characteristics may become excessively high and thus the balance between the

carboxymethyl group and the cationic group may be deranged, resulting in the physical properties of the final product becoming impaired.

[0018] Further, various alkali metal hydroxide can be appropriately used as a catalyst for the cationization reaction depending on the type of the cationization agent used, and examples of such alkali metal hydroxides include sodium hydroxide and potassium hydroxide. The amount of such a catalyst added is in a range of from 0.01 mol to 1.0 mol per 1 mol of the cationization agent in the case where the cationization agent is a quaternary epoxide, and the amount of a catalyst added is in a range of from 1.0 mol to 3.0 mol per 1 mol of the cationization agent in the case where the cationization agent is a quaternary halohydrin. If the amount of a catalyst is less than 0.01 mol (in the case of using a quaternary epoxide) or 1.0 mol (in the case of using a quaternary halohydrin), the catalytic amount may be insufficient and thus the reaction rate may decrease to an impractical level, whereas if the amount of a catalyst exceeds 1.0 mol (in the case of using a quaternary epoxide) or 3.0 mol (in the case of using a quaternary halohydrin), the effective utilization ratio of the cationization agent may be significantly reduced, presumably due to the promoted secondary reaction. Therefore, in order to adjust the proportion of the alkali metal hydroxide in the reaction system to be within the

above-specified range, the catalytic amount is adjusted by either adding an alkali metal hydroxide before or after the addition of the cationization agent or conducting neutralization with a mineral acid or an organic acid.

[0019] In the present invention, the value of CD-DS is preferably in a range of from 0.01 to 1.0. If the degree of substitution of a cationic group is out of the above-specified range, improvement effects on the adhesion promoting properties and surface improving properties may not be obtained. If the value of CT-DS is less than 0.01, the effect by the introduction of a cationic group may not be obtained, whereas if the value exceeds 1.0, the cationic characteristics may become excessively high and thus the balance between the carboxymethyl group and the cationic group may be undesirably deranged.

[0020] In particular, it is preferred that the relationship between CM-DS and CT-DS in the inventive cationized CMC should satisfy the following Formula 1. When Formula 1 is satisfied, the balance of the carboxymethyl group (anion) and the cationic group (cation) can be preferably maintained and thus various properties, such as adhesion promoting properties and surface improving properties can be improved.

$$0.01 \leq (\text{CT-DS} / \text{CM-DS}) \leq 0.5 \dots \text{Formula 1}$$

[0021] Once the carboxymethylation reaction and cationization reaction have been completed, the residual alkali metal

hydroxide is neutralized with a mineral acid or an organic acid, and the resulting product is cleansed, purified, dried and crushed by conventional methods, thereby obtaining the intended cationized CMC.

[0022] The inventive cationized CMCs can be used in various forms, examples of which include: a thickening agent; a coagulating agent; a flocculating agent; an adhesion promoter; a dispersion stabilizer; a laundry finishing agent; a muddy water regulating agent; a retention aid for paper making; a drainage improving agent; an antistatic agent for fibers and fabrics; a texture improving agent; a compounding agent for shampoos, rinses, treatments and the like; and a compounding agent for pastes, adhesive agents, inks and the like. The amount to be incorporated can be appropriately determined according to the intended use.

[0023]

[Detailed Description of Embodiments] The present invention is described in greater detail below with reference to embodiments, but is not restricted to these embodiments in any way. In the following embodiments, the term "part" indicating the incorporation amount should be construed as "part by weight".

[0024] [Embodiment 1] A solution obtained by dissolving 1270 parts of 99% isopropyl alcohol and 85.0 parts of sodium hydroxide in 192 parts of water was introduced into a twin-screw

kneader of which the rotational speed had been set at 100 rpm, and 200 parts of commercially available absolute dried dissolving pulps were then introduced into the kneader. Once the contents had been stirred and mixed at a temperature of 30 degrees Celsius for 90 minutes in order to prepare alkali cellulose, the resulting alkali cellulose was mixed under further stirring with 87.0 parts of monochloroacetic acid which had been dissolved in 150 parts of isopropyl alcohol and was heated to a temperature of 70 degrees Celsius over 30 minutes so as to be reacted for 90 minutes. Thereafter, after the addition of 5.0 parts of sodium hydroxide and 46.5 parts of a 50% aqueous solution of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride, the resulting mixture was further reacted at a temperature of 70 degrees Celsius for 120 minutes. Upon completion of the reaction, the resulting product was cleansed twice with 80% methanol, neutralized, drained, dried and crushed, thereby obtaining a cationized CMC having a CM-DS value of 0.58 and a CT-DS value of 0.051.

[0025] [Embodiment 2] A solution obtained by dissolving 680 parts of 99% isopropyl alcohol and 30.0 parts of sodium hydroxide in 85.0 parts of water was introduced into a separable flask of which the rotational speed had been set at 500 rpm, and 200 parts of commercially available absolute dried CMC (trade name "Sunrose F300HC", manufactured by Nippon Paper Industries

Co., Ltd..) were then introduced into the flask. Once the contents had been stirred at a temperature of 30 degrees Celsius for 90 minutes, the product was mixed under further stirring with 140 parts of a 50% aqueous solution of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride and was heated to a temperature of 70 degrees Celsius over 30 minutes so as to be reacted for 90 minutes. Upon completion of the reaction, the resulting product was cleansed twice with 80% methanol, neutralized, drained, dried and crushed, thereby obtaining a cationized CMC having a CM-DS value of 0.87 and a CT-DS value of 0.120.

/3

[0026] [Embodiment 3] A solution obtained by dissolving 1900 parts of 99% isopropyl alcohol and 99.0 parts of sodium hydroxide in 100 parts of water was introduced into a twin-screw kneader of which the rotational speed had been set at 100 rpm, and 200 parts of commercially available absolute dried dissolving pulps were then introduced into the kneader. Once the contents had been stirred at a temperature of 30 degrees Celsius for 90 minutes in order to prepare alkali cellulose, the resulting alkali cellulose was mixed under further stirring with 70.0 parts of acetic acid and 465 parts of a 50% aqueous solution of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride and was heated to a temperature of 70 degrees Celsius over 30

minutes so as to be reacted for 90 minutes. Thereafter, after the addition of 138 parts of sodium hydroxide and 430 parts of sodium monochloroacetate, the resulting mixture was further reacted at a temperature of 70 degrees Celsius for 120 minutes. Upon completion of the reaction, the resulting product was cleansed twice with 80% methanol, neutralized, drained, dried and crushed, thereby obtaining a cationized CMC having a CM-DS value of 1.41 and a CT-DS value of 0.313.

[0027] [Comparative Example 1] Sunrose F300HC (manufactured by Nippon Paper Industries Co., Ltd.; CM-DS 0.87) was used as a commercially available CMC.

[0028] [Comparative Example 2] A solution obtained by dissolving 2500 parts of 99% isopropyl alcohol and 199 parts of sodium hydroxide in 200 parts of water was introduced into a twin-screw kneader of which the rotational speed had been set at 100 rpm, and 200 parts of commercially available absolute dried dissolving pulps were then introduced into the kneader. Once the contents had been stirred at a temperature of 30 degrees Celsius for 90 minutes in order to prepare alkali cellulose, the resulting alkali cellulose was mixed under further stirring with 145 parts of acetic acid and 930 parts of a 50% aqueous solution of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride and was heated to a temperature of 70 degrees Celsius over 30 minutes so as to be reacted for 90 minutes. Upon completion of the reaction,

the resulting product was cleansed twice with 80% methanol, neutralized, drained, dried and crushed, thereby obtaining a cationized CMC having a CT-DS value of 0.723. With 200 parts of the resulting cationized cellulose as a starting material, a solution obtained by dissolving 1900 parts of 99% isopropyl alcohol and 99.0 parts of sodium hydroxide in 100 parts of water was introduced into the same twin-screw kneader of which the rotational speed had been set at 100 rpm. Once the contents had been mixed and stirred at a temperature of 30 degrees Celsius for 90 minutes, the resulting product was mixed under further stirring with 70.0 parts of acetic acid and 465 parts of a 50% aqueous solution of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride and was heated to a temperature of 70 degrees Celsius over 30 minutes so as to be reacted for 90 minutes. Thereafter, after the addition of 141 parts of sodium hydroxide and 460 parts of sodium monochloroacetate, the resulting mixture was further reacted at a temperature of 70 degrees Celsius for 120 minutes. Upon completion of the reaction, the resulting product was cleansed twice with 80% methanol, neutralized, drained, dried and crushed, thereby obtaining a cationized CMC having a CM-DS value of 1.41 and a CT-DS value of 1.037.

[0029] [Comparative Example 3] A solution obtained by dissolving 950 parts of 99% isopropyl alcohol and 4.5 parts of sodium hydroxide in 50 parts of water was introduced into a separable

flask of which the rotational speed had been set at 500 rpm, and 200 parts of commercially available absolute dried Na-CMC (trade name "Sunrose F300HC", manufactured by Nippon Paper Industries Co., Ltd..) were then introduced into the flask. Once the contents had been stirred at a temperature of 30 degrees Celsius for 90 minutes, the product was mixed under further stirring with 20 parts of a 50% aqueous solution of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride and was heated to a temperature of 70 degrees Celsius over 30 minutes so as to be reacted for 30 minutes. Upon completion of the reaction, the resulting product was cleansed twice with 80% methanol, neutralized, drained, dried and crushed, thereby obtaining a cationized CMC having a CM-DS value of 0.87 and a CT-DS value of 0.009.

[0030] [Comparative Example 4] A solution obtained by dissolving 711 parts of 99% isopropyl alcohol and 53.5 parts of sodium hydroxide in 89 parts of water was introduced into a twin-screw kneader of which the rotational speed had been set at 100 rpm, and 200 parts of commercially available absolute dried dissolving pulps were then introduced into the kneader. Once the contents had been stirred and mixed at a temperature of 90 degrees Celsius for 30 minutes in order to prepare alkali cellulose, the resulting alkali cellulose was mixed under further stirring with 59.0 parts of monochloroacetic acid which

had been dissolved in 120 parts of isopropyl alcohol and was heated to a temperature of 70 degrees Celsius over 30 minutes so as to be reacted for 90 minutes. Thereafter, after the addition of 12.0 parts of sodium hydroxide and 142 parts of a 50% aqueous solution of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride, the resulting mixture was further reacted at a temperature of 70 degrees Celsius for 120 minutes. Upon completion of the reaction, the resulting product was cleansed twice with 80% methanol, neutralized, drained, dried and crushed, thereby obtaining a cationized CMC having a CM-DS value of 0.35 and a CT-DS value of 0.114.

[0031] [Comparative Example 5] A solution obtained by dissolving 2500 parts of 99% isopropyl alcohol and 318 parts of sodium hydroxide in 300 parts of water was introduced into a twin-screw kneader of which the rotational speed had been set at 100 rpm, and 200 parts of commercially available absolute dried dissolving pulps were then introduced into the kneader. Once the contents had been stirred and mixed at a temperature of 90 degrees Celsius for 30 minutes in order to prepare alkali cellulose, the resulting alkali cellulose was mixed under further stirring with 450 parts of sodium monochloroacetate and was heated to a temperature of 70 degrees Celsius over 30 minutes so as to be reacted for 90 minutes. Upon completion of the reaction, the resulting product was cleansed twice with 80%

methanol, neutralized, drained, dried and crushed, thereby obtaining a Na-CMC having a CT-DS value of 1.51. With 200 parts of the resulting Na-CMC as a starting material, a solution obtained by dissolving 2810 parts of 99% isopropyl alcohol and 210 parts of sodium hydroxide in 190 parts of water was introduced into the same twin-screw kneader of which the rotational speed had been set at 100 rpm. Once the contents had been mixed and stirred at a temperature of 30 degrees Celsius for 90 minutes, the resulting product was mixed under further stirring with 298 parts of sodium monochloroacetate and was heated to a temperature of 70 degrees Celsius over 30 minutes so as to be reacted for 90 minutes. Thereafter, after the addition of 16.0 parts of sodium hydroxide and 151 parts of a 50% aqueous solution of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride, the resulting mixture was further reacted at a temperature of 70 degrees Celsius for 120 minutes. Upon completion of the reaction, the resulting product was cleansed twice with 80% methanol, neutralized, drained, dried and crushed, thereby obtaining a cationized CMC having a CM-DS value of 2.03 and a CT-DS value of 0.107.

[0032] [Testing Methods]

1) Measuring Method for Carboxymethylation Degree (CM-DS)

The value of CM-DS was obtained by the following two methods.

When the value of CM-DS was 1.0 or less, the following nitric

acid / methanol method was used, and when the value of CM-DS exceeded 1.0, the following ash alkali method was used.

<Nitric Acid / Methanol Method> Approximately 2.0 g of the sample was precisely weighed and was introduced into a 300-mL stoppered Erlenmeyer flask. 100 mL of a nitric acid / methanol mixture solution (solution obtained by adding 100 mL of reagent grade concentrated nitric acid in 1 L of anhydrous methanol) was introduced into the flask, and the resulting flask was agitated in order to convert carboxymethyl cellulose sodium (Na-CMC) into carboxy methyl cellulose (H-CMC). 1.5 g to 2.0 g of the resulting absolute dried H-CMC was precisely weighed and was introduced into a 300-mL stoppered Erlenmeyer flask. The H-CMC, which had been wetted with 15 mL of 80% methanol, was mixed with 100 mL of 0.1 N NaOH and was then agitated at room temperature for three hours. Excess NaOH was back-titrated with 0.1N H₂SO₄ by using phenolphthalein as an indicator. The value of CM-DS was calculated by the following formula.

$$A = ((100 \times F' - 0.1 \text{ N-H}_2\text{SO}_4 \text{ (mL)} \times F) \times 0.1) / \text{absolute dry weight of H-CMC (g)}$$
$$\text{CM-DS} = 0.162 \times A / (1 - 0.058 \times A)$$

A: Amount of 1N-NaOH (mL) required for neutralizing 1 g of H-CMC

F: Factor of 0.1N H₂SO₄

F': Factor of 0.1 N NaOH

<Ash Alkali Method> Approximately 0.5 g of the sample was precisely weighed, was introduced into a platinum dish and was carbonized on an electric heater. Thereafter, the resulting produce was uniformly heated for a period of from one minute to two minutes on an electric heater (at a temperature of 750 ± 25 degrees Celsius). Once the resulting product had been cooled, the solute part was extracted with warm water, and the whole amount of the extract was then introduced into a beaker while cleansing it with warm water. The warm water-soluble part was mixed with 100 mL of 0.1 N H_2SO_4 , was boiled for 10 minutes, was cooled, and then excess H_2SO_4 was titrated by using phenolphthalein as an indicator. The value of CM-DS was calculated by the following formula.

$$A = (100 \times F' - 0.1\text{N NaOH (mL)} \times F) / \text{absolute dry weight of sample (g)}$$

/4

$$\text{CM-DS} = 162 \times A / (1000 - 80 \times A)$$

F: Factor of 0.1 N H_2SO_4

F': Factor of 0.1 N NaOH

[0033] 2) Measuring Method for Cationization Degree (CT-DS)

The nitrogen content was measured by the Kjeldahl analysis method, and the value of CT-DS was calculated by the following formula. In the formula, glycidyl trimethyl ammonium halide or its halohydrin form was used as a cationization agent.

$$CT-DS = (162 + 80 \times (CM-DS)) \times B / (1400 - 133.1 \times B)$$

B: Nitrogen content

[0034] 3) Chemical Resistance Test

990 g of pure water was introduced into a 1000-mL beaker. While the solution was being stirred with a triangle stirrer, 10 g of a precisely weighed CMC (anhydride) was added thereto and was completely dissolved therein. Thereafter, the solution

temperature was adjusted at 25 ± 0.2 degrees Celsius, and the viscosity η_1 of the solution which had been stirred at a rotational speed of 30 rpm for three minutes was determined by using a BM type viscometer (manufactured by Tokyo Keiki Inc.)

990 g of a 4% saline solution was introduced into a 1000-mL beaker. While the solution was being stirred with a triangle stirrer, 10 g of a precisely weighed cationized CMC (anhydride) was added thereto and was completely dissolved therein.

Thereafter, the solution temperature was adjusted at 25 ± 0.2 degrees Celsius, and the viscosity η_2 of the solution which had been stirred at a rotational speed of 30 rpm for three minutes was determined by using a BM type viscometer (manufactured by Tokyo Keiki Inc.) Thereafter, the viscosity change, i.e., η_2/η_1 , was calculated as an indicator of the chemical resistance. The chemical resistance is better as the value of η_2/η_1 approaches 1.

[0035] 4) Surface Improvement Test

A hair cosmetic (spray) having a composition of 1,2-dimethoxyethane / stock solution that was 30 / 70 was obtained by adding 1,2-dimethoxy ethane to a stock solution (100 parts) consisting of 5 parts of the cationized CMC, 1 part of concentrated glycerol, 10 parts of ethanol, 0.1 parts of methylparaben, perfume and purified water. Once a prepared hair strand having a length of 18 cm and a weight of 10 g had been wetted with water and then dried with a towel, 2 g of the hair cosmetic was applied to the hair strand, which was wound around a rod having a diameter of 2 cm and was then naturally dried. Ten panelists evaluated the resulting hair strand in terms of the hair feel (texture) by the following rating scale:

⊙: Much better than non-applied hair;

○: Better than non-applied hair;

△: No change as compared with non-applied hair;

×: Worse than non-applied hair.

[0036] 5) Adhesion Promoting Property Test

Broad leaf unbleached kraft pulps were introduced into a laboratory Niagara beater so that the freeness was adjusted at 480 mL CSF (Canada standard freeness). While 2% pulp slurry was being stirred in a three-one motor at a rotational speed of 450 rpm, 0.2% a cationized CMC in the form of a 1% cationized CMC aqueous solution, 0.5% a cationized starch, 0.3% aluminum sulfate, 0.05% a sizing agent for natural paper consisting

chiefly of alkyl ketene dimer, 0.1% a paper strength additive containing a polyamide and epichlorohydrin resin, 10% precipitated calcium carbonate and 0.01% of a yield improver containing polyacrylamide were added in this order. Once the components had been added, the resulting mixture was further stirred for three minutes. The resulting pulp paper stock was formed into a paper sheet having a basis weight of 60 g/m² by using a TAPPI standard sheet machine, and the resulting paper sheet was dried in a drum type drier at a temperature of 120 degrees Celsius for three minutes. Once the resulting paper sheet had been adjusted at a temperature of 20 degrees Celsius and a relative humidity of 65% for 24 hours, the tensile strength (measured in accordance with TAPPI T205, expressed in the breaking length) and the Stockigt sizing degree (measured in accordance with JIS P8122) of the resulting paper sheet were measured. The greater values of both the breaking length and the Stockigt sizing degree are better, indicating that chemicals for paper making were desirably adhered to the pulps and the intended function is developed.

[0037]

[Table 1] Table 1

	Degree of Substitution			Chemical Resistance	Surface Improving Property	Adhesion Promoting Property	
	CM-DS	CT-DS	CT-DS/CM-DS	η_2/η_1	Texture	Breaking Length (km)	Stockigt Sizing Degree (sec)
E1	0.58	0.051	0.088	0.75	○	3.8	35
E2	0.87	0.120	0.138	0.81	◎	3.8	37
E3	1.41	0.313	0.222	0.77	◎	4.0	38
C1	0.87	—	—	0.57	△	3.3	20
C2	1.41	1.037	0.735	0.39	○	3.4	24
C3	0.87	0.009	0.010	0.58	△	3.2	19
C4	0.95	0.114	0.326	0.13	×	3.1	19
C5	2.03	0.107	0.0553	0.54	△	3.5	22

[0038]

[Effect of the Invention] The cationized CMC according to the present invention were excellent as an amphoteric ion polymer in terms of chemical resistance, surface improving properties, and adhesion promoting properties, and these physical properties were well balanced. Therefore, the inventive cationized CMC can be effectively used in various forms, examples of which include: a thickening agent; a coagulating agent; a flocculating agent; an adhesion promoter; a dispersion stabilizer; a laundry finishing agent; a muddy water regulating agent; a retention aid for paper making; a drainage improving agent; an antistatic agent for fibers and fabrics; a texture improving agent; a compounding agent for shampoos, rinses, treatments and the like; and a compounding agent for pastes, adhesive agents, inks and the like.

/5

[Amendment of Proceedings]

[Date Submitted] March 5, Heisei 13 (2001. 3. 5)

[Amendment 1]

[Object for Amendment] Specification

[Amendment Item] 0033

[Amendment Method] Modification

[Contents of Amendment]

[0033] 2) Measuring method for cationization degree (CT-DS)

The nitrogen content was measured by the Kjeldahl analysis method, and the value of CT-DS was calculated by the following formula. In the formula, glycidyl trimethyl ammonium chloride or its chlorohydrin form was used as a cationization agent.

$$\text{CT-DS} = (162 + 80 \times (\text{CM-DS})) \times B / (1400 - \underline{151.6} \times B)$$

B: Nitrogen content

[Amendment of Proceedings]

[Date Submitted] March 5, Heisei 13 (2001. 3. 5)

[Amendment 1]

[Object for Amendment] Specification

[Amendment Item] 0033

[Amendment Method] Modification

[Contents of Amendment]

[0033] 2) Measuring method for cationization degree (CT-DS)

The nitrogen content (%) was measured by the Kjeldahl analysis method, and the value of CT-DS was calculated by the following

formula. In the formula, glycidyl trimethyl ammonium chloride or its chlorohydrin form was used as a cationization agent.

$$\text{CT-DS} = (162 + 80 \times (\text{CM} - \text{DS})) \times \text{B} / (1400 - \underline{151.6} \times \text{B})$$

B: Nitrogen content (%)